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COMPLETE SPECIFICATION

Method of manufacturing Cis-1,4-Polybutadiene

We, BRIDGESTONE TIRE KABUSHIKI KAISHA of No. 1, 1-Chome, Kyobashi, Chuo-Ku, Tokyo, Japan, a company organized according to the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of a solid butadiene polymer having a high content or cis-1,4 configuration by contacting butadiene with a catalyst system consisting of (A) a carrier-supported oxide of nickel or cobalt, (B) a boron halide, a complex compound thereof, chloride or oxychloride of a metal of group IV-A or V-A and (C) an organometallic compound or a hydride of an alkali metal or a metal of groups II or III of the Periodic Table, or an alkali metal powder.

The Periodic Table used is that shown on page 517 of Volume 17 of the Encyclopædia Britannica (1960), entitled: "The Short-Period form of the Periodic System of the Elements," and referred to as "Table 1".

One object of our invention is to provide a novel and highly useful catalyst system for the preparation of a solid butadiene polymer having a high content of cis-1,4 configuration from butadiene. Another object is to provide a relatively low temperature, low pressure process for the polymerization of butadiene in substantial yields to form a solid butadiene polymer having a high content of cis-1,4 configuration.

In order to find a suitable catalyst for manufacturing cis - 1,4 polybutadiene, the present knowledge of ordinary or even stereospecific catalysts for the polymerization of monoolefins is almost useless, because monoolefins can not polymerize by 1,4 - addition. Even knowledge of catalysts which polymerize isoprene by cis - 1,4 - addition the catalyst to polymerize butadiene by cis - 1,4 - addition is still unpredictable, perhaps because isoprene monomer is more stable in the cis-form but butadiene is more stable in the trans-form.

For instance, triethylaluminium - titanium trichloride catalyst is suitable for manufacturing isotactic polypropylene and triethylaluminium-titanium tetrachloride catalyst is suitable for manufacturing cis-polyisoprene, but both catalysts are unsuitable for manufacturing cis-polybutadiene.

Prior to the present invention there were several known processes for polymerizing butadiene to a solid polymer having a high content of cis-1,4 configuration as follows:—

1. Phillips Process, which is a polymerization process using the catalyst system consisting of trialkyl-aluminium and titanium tetraiodide.
2. Hüls Process, which is a polymerization process using the catalyst system consisting of triisobutylaluminium and titanium tetrabromide.
3. Montecatini Process, which is a polymerization process, using the catalyst system consisting of dialkyl-aluminium chlorides and cobaltous chloride.

It has also been known in the polymerization of olefins that boron halides have the effect of promoters for a mixed catalyst of organo-aluminium compounds and a compound of a metal belonging to group IV, V or VI of the Periodic Table (Refer to British Patent No. 846,731).

This invention is based on the discovery of an unexpected fact which could not be conceived from the above described methods, i.e., the inventors, after long continued investigations of catalysts which are effective to convert butadiene to a solid polymer having a high content of cis-1,4 configuration, have found that an oxide of nickel-diatomaceous earth has such effect by itself and then that a catalyst consisting of an oxide of nickel-diatomaceous earth and triethylaluminium or boron trifluoride etherate has also a similar effect and furthermore, improved polymerization activity. The activity, however, is not

still sufficiently great. On the other hand, the catalyst system prepared by mixing the three components of an oxide of nickel-diatomaceous earth, boron trifluoride etherate and triethylaluminium as explained in the Examples showed remarkable increases not only in the polymerization activity but also in the molecular weight of the polymers obtained. This was an entirely unexpected fact.

Further, it has been proved that the present catalyst has advantages as explained hereafter if compared with those of known processes, that is, by the known process (1) using a mixed catalyst of triethylaluminium and titanium tetraiodide polymers having cis-1,4 contents of usually about 90% are provided, and only about 94% at most, and by the known process (2) using a mixed catalyst of triisobutylaluminium and titanium tetrabromide polymers having a cis-content of about 85% at the maximum are provided, and also in the process (3) using a mixed catalyst of cobaltous chloride and diethylaluminium chloride, with which the maximum content of cis-1,4 configuration in the polymer is obtainable, it is necessary to regulate the temperature of polymerization at a temperature below 25° C. in order to obtain more than 90% of cis-1,4 configuration because as the polymerization temperature becomes higher the content of cis-1,4 configuration decreases and if the polymerization is effected at 40° C. the cis-1,4 content will be reduced to 83.5% as described. On the contrary, when the catalyst system of this invention is used it is not necessary to keep the temperature of polymerization at room temperature or less in order to obtain more than 90% of cis-1,4 configuration and even when the polymerization is effected at a temperature of 40° C. or higher, more than 95% of cis-1,4 configuration of obtained polymer can be maintained. This means that the control of the exothermic polymerization reaction of butadiene is very easy and it is one of the advantageous features of the catalyst system of this invention.

The known process using boron halides as a promoter uses as a component of the catalyst a compound of any of metals of groups IV, V and VI of the Periodic Table, while this invention does not use such a compound as a catalyst component, but uses a carrier-supported oxide of nickel or cobalt, so that it is different from the catalyst of the above known process. Moreover, the essential difference is that boron halides are used for changing the activity of olefin polymerization and lowering the molecular weight of the obtained polymer in the known process, while the boron halides are used for increasing the molecular weight to an extent which could not be obtained with a catalyst of an oxide of nickel-diatomaceous earth alone or a mixture of it and an organoaluminium compound in the process of this invention. This fact shows that the present invention can not be conceived from the known process.

The present invention provides a novel process of polymerization for converting butadiene to a solid polymer having a high content of cis-1,4 configuration in the presence of the catalyst system which is essentially different from those of known processes for polymerization as above described. The butadiene polymers manufactured by the process of this invention are rubbery solids and if their microstructures are determined according to the infrared spectroscopic analysis proposed by Morero (La Chimica e L'industria, *41,* 758 (1959)), the cis-contents of them are usually more than 85%, and 95% or more when some representative catalyst component combinations are used. The polybutadiene manufactured with some representative catalyst systems of this invention usually contains no gel even when butadiene is polymerized under conditions of temperature between 0° C. and 70° C. and a high concentraiton of produced polymers.

The present invention also provides a method for preparing a novel catalyst system by mixing at a controlled temperature three kinds of indispensable components A, B and C described as follows:—

The A component is a carrier-supported oxide of a metal selected from nickel or cobalt which is prepared by dispersing said metal oxide on a carrier to give a large surface area for its weight and is used in the form of a fine powder or a porous solid. A carrier-supported oxide of nickel is used preferably in this invention because it has better polymerization activity and cis-1,4 orientating power as shown in later examples.

The B component is a metal halide selected from the class consisting of boron halides, complex compounds thereof, the halides of the metals of groups IV-A and V-A, the oxyhalides of the metals of group V-A and the derivatives obtained by substituting a monovalent hydrocarbon radical for at least one but not all of the halogen atoms of the metals of groups IV-A and V-A of the Periodic Table.

The C component is selected from organometallic compounds, or hydrides of the alkali metals or the metals of groups II or III of the Periodic Table, and alkali-metal powders.

The mixing ratios of three components A, B and C affect the polymerization activity of the catalyst system, among which the mole ratio of said C to said B component has a greater influence on the activity. Said mole ratio used in the process of this invention lies between about 0.1 and about 10 and preferably between about 0.1 and about 5. The mole ratio from 0.5 to 1.2 produces the largest polymerization activity in general. The ratio of said A to said B or C component is not

as critical as the ratio of C to B component, but the mole ratio of said metal oxide to said C component is between about 0.1 and about 10 as hereinafter described.

The present invention provides a process for polymerizing butadiene to a solid polymer having a high content of cis-1,4 configuration by using said catalyst system in liquid phase at a temperature of from $-50°$ C. to $150°$ C. and under a pressure at which the liquid phase can be maintained and in an inert atmosphere. It is preferable to effect the polymerization by using the catalyst system at a temperature of from $-5°$ C. to $70°$ C. and at one or several atmospheres pressure. The polymerization proceeds under a partial pressure of butadiene lower than 1 atmosphere.

The A component of the catalyst of this invention which is a carrier-supported nickel oxide or cobalt oxide having a large surface area for its weight may be prepared by the following methods.

One method is oxidation of any one of hydroxides, organic acid salts and inorganic acid salts of nickel or cobalt which is adhered to a carrier having a large surface area for its weight by the processes of impregnation or co-precipitation described in the literature, said oxidation being effected with oxygen or a mixture of oxygen and nitrogen at a temperature lower than $600°$ C. Examples of said organic acid are formic acid, oxalic acid, acetic acid, citric acid and tartaric acid. Examples of said inorganic acid are nitric acid, sulphuric acid and carbonic acid.

Another method is an oxidation of either carrier-supported metallic nickel or cobalt which is used for ordinary hydrogenation reactions, said oxidation being effected with a mixture of oxygen and nitrogen at a temperature lower than $600°$ C. to avoid sintering.

The carrier which is a indispensable constituent of the A component of the present catalyst system has the power to promote the effectiveness of said metal oxide. According to a comparative experiment a catalyst system comprising non-supported metal oxide was far less effective for butadiene polymerization as shown in a later example. Thus this power of the carrier makes it possible to produce successfully the catalyst system of this invention. An effective carrier of this invention has surface areas of at least 1 square metre per gram.

Said carrier-supported metal oxide usually contains said metal oxide in a proportion between about 0.5 and about 90 weight percent. Examples of said carrier are diatomaceous earth, silica, silica-alumina, titania, zirconia, active clay and kaolin. Among these diatomaceous earth is preferably used.

Examples of said B component of the catalyst system of this invention are boron trifluoride, boron trifluoride etherates, boron trichloride, boron tribromide, titanium tetrachloride, titanium tetrabromide, titanium trichloride, zirconium tetrachloride, vanadium tetrachloride, vanadium oxychloride, alkyltitanium trichlorides and dicyclopentadienyl titanium dichloride.

Examples of said C component of the catalyst system of this invention are:

trialkylaluminium, dialkylaluminium halides, alkylaluminium dihalides, trialkylboron, dialkylmagnesium, dialkylzinc, dialkylcadmium, alkylmagnesium halides, arylmagnesium halides, alkyllithium, alkylsodium, alkylpotassium, aluminium hydride, boron hydride, calcium hydride, lithium hydride, sodium hydride, lithium aluminium hydride, lithium boron hydride, aluminium boron hydride, lithiumaluminiumtetraalkyl, sodium powder and potassium powder.

The three component catalyst system of this invention is prepared by mixing together said A, B and C components in liquid phase at a controlled temperature of from $-100°$ C. to $+150°$ C. depending on the selected component combination. Said liquid phase is preferably selected from inert anhydrous liquid hydrocarbons.

When the B component is boron trifluoride or boron trifluoride etherate, it is preferable that said B component is mixed with said carrier-supported metal oxide ssupended in an anhydrous liquid hydrocarbon diluent and then the mixture is heat-treated at a temperature between about $10°$ C. and about $100°$ C. The heat-treated mixture is then mixed with said C component after it is cooled to a temperature between about $30°$ C. and about $-80°$ C.

On the other hand, when the B component is titanium tetrachloride and the C component is trialkylaluminium, both being soluble in the hydrocarbon, it is preferable that the three components A, B and C are mixed together in the described order at a temperature between about $-100°$ C. and about $40°$ C. in the liquid hydrocarbon solvent. If the C component is said metal hydride or metal powder, which is insoluble in the hydrocarbon, it is preferable to mix together the three components at a higher temperature ranging from about $40°$ C. to about $100°$ C. in the liquid hydrocarbon.

In general it is necessary to mix the three components as uniformly as possible by the operation of dissolving, dispersing, stirring or shaking to obtain effective reaction of the components.

As above described, the activity of the catalyst system of this invention to polymerize butadiene depends on the order of mixing of the catalyst components, the reaction temperature and the reaction time. These facts reveal that the catalyst system of this invention is not a simple mixture of three com-

ponents, but a reaction product consisting of three components which are combined indispensably. Various modifications concerning the method of catalyst preparation may be utilized for control of the polymerization reaction.

Preferably the following combinations of catalyst components are used in this invention as is shown in later examples: an oxide of nickel-diatomaceous earth—boron trifluoride etherate—triethylaluminium, an oxide of nickel-diatomaceous earth—boron trifluoride etherate—butyllithium, an oxide of nickel-diatomaceous earth—titanium tetrachloride—triethylaluminium, an oxide of nickel-diatomaceous earth—titanium tetrachloride—butyllithium and an oxide of nickel-diatomaceous earth—titanium tetrabromide—triethylaluminium.

It is desirable to minimize the introduction of water, oxygen, alcohol and acid into contact with the catalyst, but the effect of these materials on the polymerization activity and cis-1,4 orientating activity of the catalyst system is not as sensitive as that of Ziegler-type catalysts.

Solvent is generally used to control the polymerization easily, but of course the polymerization can be effected without solvent, the volume ratio of solvent to monomer being not so critical, but usually less than 40.

Solvents used in this invention are hydrocarbons or halogen substituents thereof belonging to substantially dehydrated aromatic, alicyclic or aliphatic groups, for instance, benzene, toluene, xylenes, cyclohexane, heptane, pentane, petroleum ether, carbon tetrachloride, chlorobenzene or a mixture having such components. Among these, benzene, toluene or a xylene is preferable. Instead of using solvents non-reacted butadiene may be used as a diluent.

The catalyst system of this invention has powerful polymerization activity and only 0.1 mole of the C component in the catalyst system per 1000 moles of butadiene monomer is sufficient to effect polymerization in the representative combinations of the catalyst components. Thus the catalytic conversion of butadiene can be effected by various known types of polymerization process, wherein a suspension catalyst or a stationary bed or moving bed catalyst is used.

The reaction product of polymerization is usually completely dissolved in the solvent and solids in the catalyst precipitate gradually. In this case, the separation of polymer solution not containing solids can be easily done by means of a siphon or filtration. When, however, the viscosity of the solution is too high, more solvent should be added to the solution to lower the viscosity of the solution to a suitable value and solids should be completely separated by means of a siphon, filter or a centrifuge. The polymer solution free from solids is concentrated by vacuum evaporation at room temperature and after the solution has been sufficiently concentrated it is poured into a large amount of a lower alcohol to decompose and eliminate the soluble part of the catalyst and at the same time to precipitate the polymer.

In this case an antioxidant is mixed uniformly in the polymer, then the polymer is dried in vacuo at room temperature.

Butadiene polymers manufactured by the method of this invention are rubbery solids. When the intrinsic viscosity of these polymers is measured as a toluene solution at 25° C., it is usually in the range of 1.0 to 5.0. The gel contents of these polymers are usually small when measured by filtering their toluene solutions with 200 meshes wire gauze, while it is substantially zero in the polymer obtained by a catalyst system containing a boron trifluoride ether complex as a B component.

The function of the components B and C of this invention is essentially different from the function of the mixture of the B and C components alone on the polymerization of butadiene. The polymerization of butadiene by the mixture of the B and C components had already been investigated over a wide range (refer to, for instance, N. G. Gaylord, H. F. Mark, Linear and Stereoregular Addition Polymers, Interscience Publishers, (1959)). For instance, with titanium tetrachloride—triethylaluminium, if Ti/Al is 0.5:1 to 1.5:1 mole ratio, a mixture of cis-1,4 polybutadiene and trans-1,4 polybutadiene (the content of cis-1,4 configuration for the total polybutadiene is less than 70%) is obtained and if the ratio is 1.5:1 to 3:1, more particularly 2:1, substantially all trans-1,4 polybutadiene is obtained. With a mixed catalyst of titanium trichloride, vanadium trichloride or vanadium oxychloride and organometallic compounds of aluminium or zinc, trans-1,4-rich polybutadiene is obtained. In general, with the mixed catalyst of the chlorides of metals in IV-A group and V-A group in the Periodic Table and organometallic compounds, trans-1,4-rich polybutadiene is obtained more often, as is well known.

The polymerization of the method of this invention is based on the discovery that the carrier-supported oxide of group VIII metal has strong cis-1,4 orientation, independent of the orientating properties of B-C mixture. Even if, for instance, the B-C combination which has strong trans-1,4 orientation ability is employed as the two component system in the method of this invention it only serves mainly as a promoter. However, the catalyst of this invention using oxidized nickel-diatomaceous earth, titanium tetrachloride and triethylaluminium as A, B and C respectively (mole ratio of B/C is 1) provides poly-

butadiene having more than 90% cis-1,4 content.

EXAMPLE 1

Similarly to the method of manufacturing metallic nickel-diatomaceous earth catalysts to be used for ordinary hydrogenation reaction, basic nickel carbonate was precipitated on diatomaceous earth by mixing nickel sulphate and sodium carbonate in a dispersion of diatomaceous earth in water, and after drying, the carbonate on the carrier was thermally decomposed at 350° C. by passing air and then reduced at 360° C. by passing hydrogen. The metallic nickel-diatomaceous earth (nickel content: 50%) thus obtained was brought into contact with gas which consisted of air diluted with a large quantity of nitrogen to be stabilized and then oxidized at 480° C. for 5 hours by passing air. The oxide of nickel - diatomaceous earth thus obtained was a black powder.

A given quantity of the oxide of nickel-diatomaceous earth, 40 ml. of purified benzene dehydrated by metallic sodium, a given quantity of titanium tetrachloride and a given quantity of triethylaluminium were successively introduced in a pressure bottle of 180 ml. capacity, while flushing purified nitrogen gas therein and shaking the bottle. After the pressure bottle was cooled to −20° C., 25 ml. of liquefied butadiene dried with caustic potash and calcium chloride then dehydrated by cooling to −78° C. was poured in the bottle. The bottle was tightly sealed and revolved for agitation in a thermostat at 40° C. for a certain time at a speed of 40 r.p.m., then the bottle was opened and unreacted butadiene was expelled. 100 ml. of benzene were added to the residual solution and after being well-shaken the mixture was allowed to stand for a short time to precipitate the solid parts of the catalyst system. The supernatant liquid was then removed and a small amount of suspended catalyst solids was eliminated completely from it by centrifuging and then it was poured in a large amount of methanol containing an antioxidant to precipitate the polymer and at the same time to decompose the soluble portion of the catalyst. The polymer was dried in vacuo at room temperature and was a white rubbery solid. Its microstructure was determined according to the Morero method and its intrinsic viscosity was measured at 25° C. in toluene solution.

For the sake of comparison, the polymerization reactions using an oxide of nickel-diatomaceous earth alone, and an oxide of nickel-diatomaceous earth—triethylaluminium were effected. Also the polymerization reactions using the catalyst system comprising non-supported nickel oxide are effected in the same manner with No. 1 and 2. (Commercial nickelous oxide or nickelic oxide).

No.	An oxide of nickel-diatomaceous earth (g.)	Titanium tetrachloride (mmoles)	Triethyl-aluminium (mmoles)	Polymerization time (hr.)
1	1.0	1.0	1.0	1.5
2	2.0	1.0	1.0	1.5
Reference				
1	5.0	—	1.0	3.5
2	10.0	—	—	4.0
3	NiO 2.0	1.0	1.0	5.0
4	Ni_2O_3 2.0	1.0	1.0	5.0

No.	Polymer yield (g.)	Microstructure (%)			Intrinsic viscosity
		cis-1,4	trans-1,4	Vinyl	
1	7.8	92.6	3.9	3.5	1.0
2	5.3	94.6	2.6	2.8	1.7
Reference					
1	2.6	94.4	3.0	2.6	—
2	2.4	94.2	3.4	2.4	1.4
3	less than 0.1	—	—	—	—
4	less than 0.1	—	—	—	—

EXAMPLE 2

Nickel carbonate was precipitated on diatomaceous earth by mixing nickel nitrate and sodium bicarbonate in a dispersion of diatomaceous earth in water and the carrier-supported nickel carbonate was thermally decomposed by oxidation at 450° C. for 10 hours by passing air. The oxide of nickel-diatomaceous earth thus obtained comprised 10% of nickel and showed dark brown colour. Butadiene was polymerized in a similar manner as Example 1 except that the catalyst system prepared by mixing oxidized nickel suspended in 40 ml. of benzene, titanium tetrachloride and triethylaluminium in th described order at −50° C., was used.

No.	Oxide of nickel-diatomaceous earth (g.)	Titanium tetrachloride (mmoles)	Triethyl-aluminium (mmoles)	Polymerization time (min.)	Polymer Yield (g.)
1	2.0	1.0	1.0	70	9.8
2	4.0	1.0	1.0	70	12.2
3	2.0	1.0	0.5	70	8.8

No.	Microstructure (%)			Appearance of Polymer
	cis-1,4	trans-1,4	Vinyl	
1	90.3	5.7	4.0	transparent rubbery solid
2	91.2	5.1	3.7	"
3	89.4	6.7	3.9	

EXAMPLE 3

A similar experiment to that of Example 2 was effected by using 40 ml. of purified toluene instead of solvent benzene, and 11.5 g. of transparent rubbery solid polymer was obtained. The microstructure of this polymer was 89.3% of cis-1,4, 6.8% of trans-1,4 and 3.9% of vinyl configurations.

EXAMPLE 4

Butyllithium or diethylcadmium was used as another example of the C component of the catalyst system of this invention, and titanium tetrabromide or vanadium oxychloride was used as another example of the B component. Butadiene was polymerized with the catalyst system prepared by combining these compounds with an oxide of nickel-diatomaceous earth (Ni content 10%) at −50° C. in the same manner as Example 2.

No.	Oxide of nickel-diatomaceous earth (g.)	C component (mmoles)	B component (mmoles)	Polymerization time (hr.)
1	2.0	butyllithium 1.0	titanium tetrachloride 1.0	5.0
2	2.0	diethylcadmium 1.0	titanium tetrachloride 1.0	5.0
3	2.0	triethylaluminium 1.0	titanium tetrabromide 1.0	1.2
4	2.0	triethylaluminium 1.0	vanadium oxychloride 1.0	18.5

No.	Solvent (ml.)	Polymer yield (g.)	Microstructure (%)		
			cis-1,4	trans-1,4	Vinyl
1	Benzene 40	1.5	91.6	5.9	2.5
2	”	0.8	88.4	7.2	4.4
3	”	11.2	89.3	7.0	3.7
4	Toluene 40	0.8	88.8	7.9	3.3

EXAMPLE 5

Cobalt carbonate was precipitated on diatomaceous earth by mixing cobalt nitrate and sodium bicarbonate in a dispersion of diatomaceous earth in water, and the carrier-supported cobalt carbonate thus obtained was thermally decomposed by oxidation at 480° C. for 5 hours in air. The oxide of cobalt-diatomaceous earth thus obtained was a black powder containing 50% of cobalt. Butadiene was polymerized in the same manner as Example 2 by using an oxide of cobalt-diatomaceous earth instead of an oxide of nickel-diatomaceous earth. The polymer thus obtained was a transparent rubbery solid.

No.	Oxide of cobalt-diatomaceous earth (g.)	Titanium tetrachloride (mmoles)	Triethylaluminium (mmoles)	Polymerization time (hr.)
1	2.0	1.0	1.0	3.0
2	2.0	1.5	1.0	3.0
3	2.0	2.0	4.0	0.2

No.	Polymer yield (g.)	Microstructure (%)		
		cis-1,4	trans-1,4	Vinyl
1	2.3	93.1	6.1	0.8
2	3.6	87.6	8.8	3.6
3	3.0	93.6	4.9	1.5

EXAMPLE 6

Diatomaceous earth was dispersed in an aqueous solution of nickel nitrate and 10% solution of sodium carbonate was gradually fed drop-by-drop therein. Basic nickel carbonate was precipitated on the diatomaceous earth, and the precipitate was washed with water, dried, and oxidized at 450° C. for 5 hours by passing dry air. The oxide of nickel-diatomaceous earth thus obtained was a greyish black powder containing about 10% nickel.

60 ml. of purified benzene was put in a pressure bottle while flushing purified nitrogen and 1 g. of said oxide of nickel-diatomaceous earth was dispersed therein, and then 2.0 mmoles of boron trifluoride etherate was added thereto and the mixture was heated at 40° C. for 1 hour with stirring and after cooling to room temperature, 2.0 mmoles of triethylaluminium was added to prepare the catalyst system. The bottle was cooled to −10° C. and 25 ml. of liquefied butadiene was poured in it. Then the bottle was tightly sealed and subjected to revolution at 40 r.p.m. for stirring in a thermostat at 40° C. for 70 minutes, and then a small quantity of methanol was poured in the bottle to stop the polymerization. Since the polymer thus obtained had entirely dissolved in benzene, the solution was suitably diluted and the solid components of catalyst were eliminated by centrifuge and after some antioxidant was added, the solution was poured into methanol. After drying the precipitate in vacuo at room temperature, 7.5 g. of transparent rubbery solid was obtained. The microstructure was analyzed according to the Morero method and the intrinsic viscosity was measured as a toluene solution at 25° C.

The results are as follows:—

Analysis of microstructure:

cis-1,4	97.3%
trans-1,4	1.6%
vinyl	1.1%

Intrinsic viscosity:

$$[\eta]^{25^\circ C.}_{toluene} \quad 4.35$$

EXAMPLE 7

2.0 mmoles of triethylaluminium, 2.0 mmoles of boron trifluoride etherate and 2 g. of the same oxide of nickel-diatomaceous earth as in Example 6 were put in 40 ml. of benzene at room temperature in the above described order to prepare the catalyst. Then 25 ml. of liquefied butadiene was poured in and the same polymerization test as Example 6 was carried out at 40° C. for 2 hours. The results were as follows:—

Yield of purified polymer: 2.2 g.

Analysis of microstructure:

cis-1,4	97.8%
trans-1,4	1.8%
vinyl	0.4%

EXAMPLE 8

An oxide of cobalt-diatomaceous earth was prepared from cobalt nitrate by the same procedure as that used in the preparation of an oxide of nickel-diatomaceous earth. This substance was a black powder containing about 50% of cobalt. 1 g. of the oxidized cobalt-diatomaceous earth was dispersed in 40 ml. of benzene and 2.0 mmoles of boron trifluoride etherate was added thereto. The mixture was heated at 40° C. for 1 hour, cooled to room temperature, and 2.0 mmoles of triethylaluminium added to prepare the catalyst system. 25 ml. of liquefied butadiene was poured therein and polymerized at 40° C. for 15 hours. After purification and drying, 3.5 g. of rubbery polymer was obtained. Microstructure: 91.5% of cis-1,4, 4.5% of trans-1,4 and 4.0% of vinyl configurations.

EXAMPLE 9

The process of Example 6 was repeated, but the triethylaluminium was replaced by 2.0 mmoles of butyllithium. The results were as follows:

Yield of purified polymer: 7.0 g.

Analysis of microstructure:

cis-1,4	94.6%
trans-1,4	2.0%
vinyl	3.4%

EXAMPLE 10

The process of Example 6 was repeated, but the triethylaluminium was replaced by 4 mg-atoms of sodium dispersed in 1 ml. of xylene and 4 mmoles of boron trifluoride was used and polymerization time was 20 hours. The results were as follows:—

Yield of purified polymer: 5.8 g.

Analysis of microstructure:

cis-1,4	89.2%
trans-1,4	7.4%
vinyl	3.4%

EXAMPLE 11

2 g. of the same oxide of nickel-diatomaceous earth as used in Example 1 dispersed in 40 ml. of benzene and 2 mmoles of titanium tetrachloride were mixed together and the mixtures were heat-treated for 1 hour at 40° C. with constant stirring and then 8 mmoles of lithium boronhydride was added to the mixture at room temperature. The catalyst system thus prepared was used for butadiene polymerization, wherein 20 ml. of liquid butadiene was used and the polymerization temperature was 40° C. and the polymerization time was 20 hours. The results were as follows:—

Yield of purified polymer: 2.1 g.

Analysis of microstructure:

cis-1,4	90.9%
trans-1,4	6.2%
vinyl	2.8%

WHAT WE CLAIM IS:—

1. A process for polymerization of butadiene, characterized in that butadiene is polymerized in liquid phase at a temperature

between about $-50°$ C. and about $+150°$ C. and under a pressure sufficient to maintain the reaction system in liquid phase and under an inert atmosphere and is converted to a solid polymer having a high content of cis-1,4 configuration by contacting butadiene with a catalyst system obtained by mixing at a controlled temperature three components consisting of (A) a carrier-supported metal oxide selected from nickel oxides and cobalt oxides in the form of a fine powder or a porous solid and (B) a halide selected from boron halides, complex compounds thereof, the halides of the metals of groups IV-A and V-A, the oxyhalides of the metals of group V-A and the derivatives obtained by substituting a hydrocarbon radical for at least one but not all of the halogen atoms of a halide of a metal group IV-A of the Periodic Table and (C) a compound selected from organometallic compounds and hydrides of the alkali-metals, and the metals of groups II and III of the Periodic Table, and alkali-metal powders.

2. A process according to claim 1, characterized in that butadiene is polymerized in a liquid hydrocarbon diluent by contact with said catalyst system, wherein the mole ratio of said C component to said B component is from 0.1 to 10, said C component being used in a ratio of more than 0.1 mole per 1000 moles of butadiene monomer.

3. A process according to either of claims 1 or 2, wherein said carrier is selected from diatomaceous earth, silica-alumina, silica, titania, zirconia, active clay and kaolin.

4. A process ccording to any of claims 1, 2, or 3, wherein said B component is selected from boron trihalides, boron trihalide etherate, titanium tetrahalides and vanadium oxytrihalides.

5. A process according to any of the preceding claims, wherein said C component is an organometallic compound of a metal selected from lithium, sodium, potassium, magnesium, zinc, cadmium, boron and aluminium.

6. A process according to any of the preceding claims, wherein said carrier-supported metal oxide is prepared by oxidizing any of hydroxides, inorganic salts and organic salts of said metals adhered to the carrier with air at a temperature lower than 600° C.

7. A process according to any of claims 1 to 5, wherein said carrier-supported metal oxide is prepared by oxidizing any carrier-supported metallic nickel or cobalt which is used for ordinary hydrogenation reactions, oxidation being effected with a mixture of oxygen and nitrogen at a temperature lower than 600° C.

8. A process according to any of the preceding claims, wherein the mole ratio of said C component to said B component is between about 0.1 and about 5 and the mole ratio of said metal oxide to said C component is from 0.1 to 10.

9. A process according to any of the preceding claims, wherein said catalyst system is prepared by admixing said three components in an anhydrous liquid hydrocarbon diluent at a temperature of from $-100°$ C. and $+150°$ C.

10. A process according to any of the preceding claims, wherein said butadiene is polymerized in a substantially anhydrous liquid hydrocarbon diluent at a temperature of from $-5°$ C. to $+70°$ C. under a pressure sufficient to maintain the reaction system in liquid phase.

11. A process according to any of the preceding claims, wherein said carrier-supported metal oxide is a carrier-supported nickel oxide.

12. A process according to any of claims 2, 9 and 10, wherein said liquid hydrocarbon diluent is selected from benzene, toluene and a xylene.

13. A process according to any of claims 1, 2, 3, 6 and 7, wherein said carrier is diatomaceous earth.

14. A process according to any of the preceding claims, wherein said C component is selected from the alkylmetals consisting of trialkylaluminium and alkyllithium in which the alkyl group contains less than eleven carbon atoms.

15. A process according to any of the preceding claims, wherein said B component is selected from titanium tetrachloride and titanium tetrabromide.

16. A process according to any of claims 1 to 14, wherein said B component is selected from boron trifluoride and boron trifluoride etherate.

17. A process according to any of claims 1 to 3, 5 to 14 and 16, wherein said catalyst system is prepared by the procedure in which said B component selected from boron trifluoride and boron trifluoride etherates is mixed with said carrier-supported metal oxide suspended in an anhydrous liquid hydrocarbon diluent and then the mixture is heat-treated at a temperature of from 10° C. to 100° C. and after the heat-treated mixture is cooled to a temperature of from 30° C. to $-80°$ C. it is mixed with said C component selected from organometallic compounds of said metals.

18. A process according to any of claims 1 to 3, 5 to 14 and 16, wherein the catalyst system is prepared by the procedure in which the B component selected from titanium tetrachloride, titanium tetrabromide and vanadium oxychloride is mixed with said carrier-supported metal oxide suspended in an anhydrous liquid hydrocarbon diluent at a temperature of from $-100°$ C. to 40° C. and then the C component selected from trialkylaluminiums is added to the above mixture

at a temperature in the same range.

19. A process according to any of the preceding claims, wherein said butadiene polymer to which butadiene is converted contains more than 90 percent of cis-1,4 configuration.

20. A process according to any of claims 1 to 15, 18 and 19, wherein said catalyst system consists of an oxide of nickel-diatomaceous earth, titanium tetrachloride and trialkylaluminium in which said alkyl group contains less than eleven carbon atoms.

21. A process according to any of claims 1 to 15 and 18, wherein said catalyst system consists of an oxide of nickel-diatomaceous earth, titanium tetrabromide and a trialkylaluminium in which said alkyl group contains less than eleven carbon atoms.

22. A process according to any of claims 1 to 14, 16, 17 and 19, wherein said catalyst system consists of an oxide of nickel-diatomaceous earth, boron trifluoride etherate and an alkyllithium in which said alkyl group contains less than eleven carbon atoms.

23. A process according to any of claims 1 to 14, 16 and 19, wherein said catalyst system consists of an oxide of nickel-diatomaceous earth, boron trifluoride etherate and trialkylaluminium in which said alkyl group contains less than eleven carbon atoms.

24. A process according to any of claims 19 to 23, wherein said butadiene polymer to which butadiene is converted contains more than 95 percent of cis-1,4 configuration.

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